STUDIES ON THE POLYMERIZATION OF METHACRYLONITRILE

BY

RALPH GARDNER BEAMAN

A. B., Dartmouth College, 1943

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1948

URBANA, ILLINOIS

1948

STUDIES ON THE POLYMERIZATION OF METHACRYLONITRILE

BY

RALPH GARDNER BEAMAN

A. B., Dartmouth College, 1943

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1948

URBANA, ILLINOIS

1948

ACKNOWLEDGMENT

The author would like to express his most sincere appreciation to Professor C. S. Marvel for suggesting this study and for his advice and many helpful suggestions during the course of this work.

The writer is indebted to the Allied Chemical and Dye Corporation for the fellowship under which most of this investigation was carried out.

R. UNIV. BIBLIOTHEEK LEIDEN

STUDIES ON THE POLYMERIZATION OF METHACRYLONITRILE

Introduction

The polymerization of vinyl compounds to high molecular weight products has been the subject of a great deal of investigation from both a practical and a theoretical viewpoint. Much attention has been given recently to linear polymers because of superior characteristics and because they admit of more exact theoretical treatment.

The usual method for polymerization has been by "acid" reagents or by catalysts or conditions giving rise to free radicals[1]. Although base-catalyzed polymerization is known, little attention has been given to this method except in the case of sodium-catalyzed BUNA rubbers[2].

The purpose of the research was to investigate base-catalyzed polymerization of methacrylonitrile, both as a means for obtaining a linear product and to extend the knowledge of the mechanisms of vinyl polymerizations.

Discussion of Results

Slow polymerization of methacrylonitrile has been effected by sodium methoxide and sodium *tert.*-butoxide at room temperature, and in the case of sodium *tert.*-butoxide polymerization occurred violently at reflux temperature.

Butylmagnesium bromide or phenylmagnesium bromide reacted instantly even at —70° to effect partial polymerization to products of molecular weight of about 8,000. Triphenylmethylsodium gave similar results except that the product was of a higher degree of polymerization as shown by viscosity determinations.

Sodium in liquid ammonia effected immediate and quantitative polymerization to a polymer of molecular weight

over 100,000. The scope of this reaction was investigated by the use of seven other vinyl compounds. Isobutylene and butadiene gave no polymer. Partial polymerization to low-molecular weight products was observed with styrene. Ethyl acrylate and vinyl acetate gave viscous oils. Acrylonitrile and methyl methacrylate were immediately and quantitatively polymerized to solid products.

The polymethacrylonitrile obtained by these methods was shown to resemble closely that obtained by peroxide catalysis[3] by means of analyses, behavior when heated, solubility, viscosity of dilute solutions, and hydrolysis to polymethacrylic acid.

It is proposed that in each case polymerization is initiated by a negative fragment and that propagation is effected by an anionic chain mechanism. Rapid polymerization at very low temperatures, the nature of the catalysts employed, and reaction in the presence of hydroquinone are cited as evidence for an ionic mechanism.

BIBLIOGRAPHY

1. Price, Abstract 112th Meeting, Am. Chem. Soc., (1947) p. 1E.
2. Ziegler, Chem. Ztg., **62,** 125 (1938).
3. Kern and Fernow, J. prakt. Chem., **160,** 296 (1942). (Translation) Rubber Chem. Tech.. **18,** 267 (1945).

VITA

The writer was born on March 10, 1923, in Plymouth, Massachusetts. He attended the public schools there through the first two years of high school. He then attended Staunton Military Academy, Staunton, Virginia, to complete his preparatory training and graduated in June, 1940. He entered Dartmouth College that fall and was granted the A. B. degree from that institution in June, 1943. He worked for a short time on the antimalarial program at Dartmouth that summer. He entered the University of Illinois Graduate School in the fall of 1943 on the Fred De Merritte Barker Fellowship from Dartmouth. He was a Special Research Assistant on the Rubber Research Program at Illinois for several months during the summer of 1944, prior to being sent on active duty as an ensign in the Naval Reserve. He was released to inactive duty with the rank of lieutenant (junior grade) in August, 1946. He re-entered the graduate school that fall and held a part-time assistantship on the Rubber Research Program until June, 1947. He held the Allied Chemical and Dye Corporation Fellowship from June, 1947, to February, 1948.

Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41549818_0255